

The University of Chicago

THE
MOLECULAR REARRANGEMENT
OF 1,1,1 DIMETHYLHYDROXY-2, 2
DIETHYL-2-AMINO ETHANE

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By
PHILIP JOHN EHMAN

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1938

The University of Chicago

THE
MOLECULAR REARRANGEMENT
OF 1,1,1 DIMETHYLHYDROXY-2, 2
DIETHYL-2-AMINO ETHANE

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By
PHILIP JOHN EHMAN

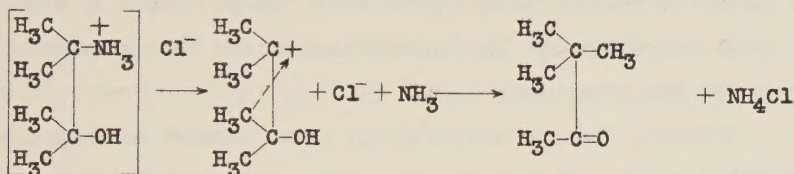
Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1938



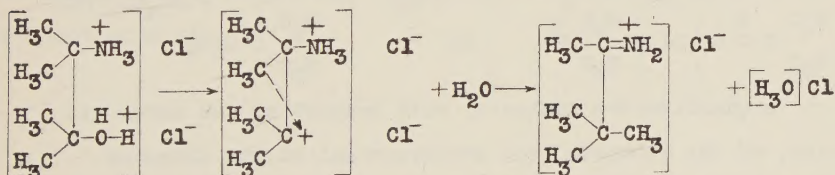
I. INTRODUCTION

In a study of the rearrangement of tetramethyl-2-amino ethanol hydrochloride, Dr. K. H. Adams¹ started from the assumption that the rearrangement would occur in the following manner:



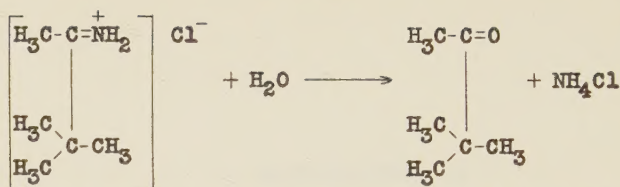
On the basis of this assumption hydrochloric acid in excess of that required to neutralize the alkamine would produce little if any acceleration in the rate of rearrangement. Contrary to this prediction he found that hydrochloric acid in excess does decidedly accelerate the rearrangement.

It was at once evident that the action of the acid on the carbinol group must lead to a rearrangement running concurrently with the rearrangement through the amine group. In the presence of free acid, the oxonium salt of the alcohol would be formed and could bring about an ordinary pinacol rearrangement as exemplified in the following manner:



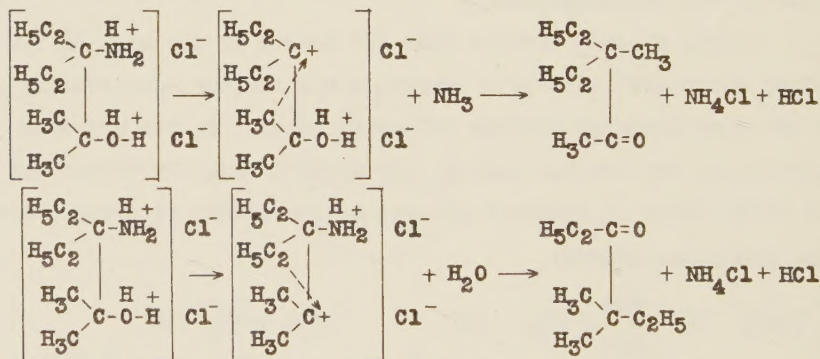
The ketimine hydrochloride would immediately undergo hydrolysis to pinacolone:

¹Adams, Doctorate Dissertation, The University of Chicago (1932).



In the case of alkamines in which the four substituent groups are the same, as in tetramethyl-2-amino ethanol, the product by rearrangement at the hydroxyl group would be identical with that formed by rearrangement at the amino group. Hence no statement could be made as to the distribution of the rearrangement between the two reactions.

However, with an unsymmetrical amino alcohol such as 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane, $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{C}_2\text{H}_5)_2\text{NH}_2$, scission at the carbon-nitrogen bond should give methyldiethylmethyl methyl ketone and with scission at the carbon-oxygen bond, dimethylethylmethyl ethyl ketone should result, according to the following scheme:

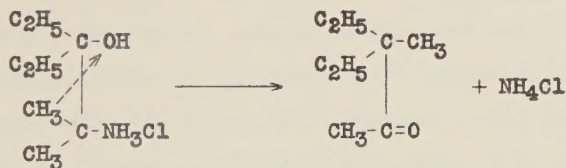


A quantitative analysis, with respect to the above two ketones, of the products from rearrangement of the alkamine hydrochloride in water solution and in acid solution should then give an indication as to where the rearrangement is occurring.

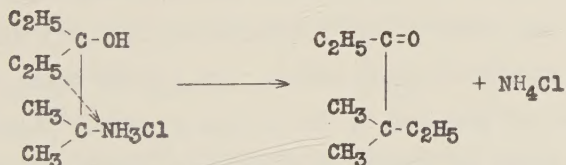
With such a view in mind the rearrangement of 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane hydrochloride in neutral

and acid solution was undertaken under the guidance and criticism of Professor Julius Stieglitz and Dr. Kenneth H. Adams.

Dr. Adams had started an investigation of the isomeric alkamine, 1,1,1 diethylhydroxy-2,2 dimethyl-2-amino ethane, which he had not completed up to the time of publication of this dissertation. His objective was the same as that outlined above. His preliminary results showed a rearrangement of the hydrochloride in aqueous and acid solution of about 30%. Rearrangement of the hydrochloride in aqueous solution seemed to occur chiefly at the carbinol-carbon atom:



although some rearrangement also took place at the amino-carbon atom:

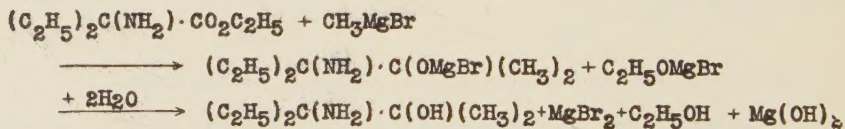


The results of rearrangement of the hydrochloride in acid solution were not complete.

III. DISCUSSION

In preparation for the study of the rearrangement of 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane, $(\text{CH}_3)_2\text{C}(\text{OH}) \cdot \text{C}(\text{NH}_2)(\text{C}_2\text{H}_5)_2$, a semi-quantitative determination of the two ketones which would be formed, was undertaken. These two ketones are dimethylethylmethyl ethyl ketone, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{C} \cdot \text{COC}_2\text{H}_5$, and methyldiethylmethyl methyl ketone, $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{C} \cdot \text{COCH}_3$. A curve of the melting-points of mixtures of the semicarbazones of the two ketones was prepared, which made it possible to estimate the proportion of the two semicarbazones, in mixtures, with an accuracy of about two per cent. The yields of the semicarbazones from the pure ketones, under identical set conditions, were then determined and found to be reproducible and accurate within about three per cent. These data made it possible thus to analyze mixtures of the two ketones with an accuracy of approximately five per cent.

For the study of the rearrangement of 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane, $(\text{CH}_3)_2\text{C}(\text{OH}) \cdot \text{C}(\text{NH}_2)(\text{C}_2\text{H}_5)_2$, the alkamine was prepared by the action of methyl magnesium bromide on the ethyl ester of α -amino diethyl acetic acid and hydrolysis of the resulting magnesium alcoholate:

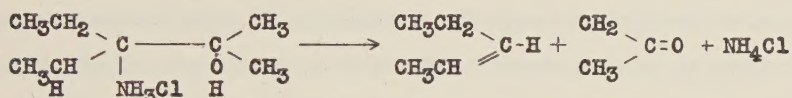


For the rearrangement of the alkamine its hydrochloride was heated in solution in twice its weight of water for seven hours at 195° - 200° . The product formed was an oil, the examination of which showed that besides rearrangement in two directions,

with the formation of the two ketones discussed above, a variety of other products, hydrocarbons, lower ketones, etc., were formed. The chief products identified were as follows:

(1) 2,3-n-Amylene. - This compound was present in very small amount, forming approximately five per cent of the oily layer. It was identified by micro-combustion (Pregl), a molecular weight determination (Victor Meyer) and oxidation at the double bond with cold, neutral and alkaline, potassium permanganate.

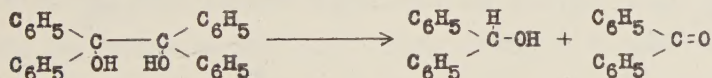
This amylene might have been formed by a scission of the molecule according to the following scheme:



A primary dissociation of the alkamine into acetone and diethyl methyl amine hydrochloride is indicated, comparable to other dissociations of the two tertiary carbon atoms, with attendant oxidation and reduction. Thus, Bettzieche and Ehrlich³⁴ observed the scission of the molecule of 1,1,1 diphenylhydroxy-2 phenyl-2-amino ethane into benzyl amine and benzophenone:



and Thorner and Zincke³⁵ observed the decomposition of tetraphenyl pinaacol into benzophenone and benzhydrol:



No evidence of the primary formation of diethyl methyl ammonium chloride was obtained. It is entirely possible, that under the conditions used the hydrochloride would lose ammonium

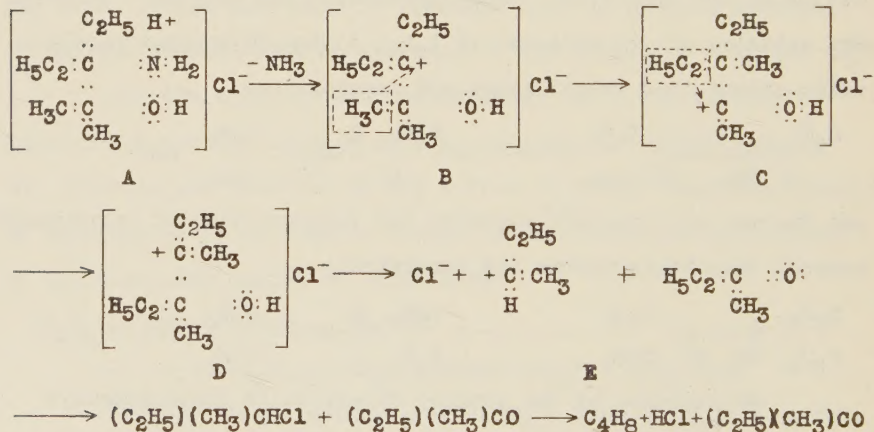
³⁴Bettzieche and Ehrlich, Z. physiol. chem., 150, 191 (1925).

³⁵Thorner and Zincke, Ber., 10, 1474 (1877).

chloride to form amylene. It is also possible, but less likely, that ammonium chloride is first lost and that the scission of the molecule follows.

(2) Acetone. - According to the reaction given above one would expect to find acetone and such was the case. It was identified by means of its p-nitrophenylhydrazone. The yield of acetone was approximately the same as that of amylene, which further tends to support the reaction mechanism as given.

(3) Methyl ethyl ketone. - A small amount, approximately five per cent, of methyl ethyl ketone was identified by means of its p-nitrophenylhydrazone. The production of this ketone is most surprising; it may represent a new kind of rearrangement of the general pinacol type, the character of which would nevertheless lie well within the framework of the general theory we are investigating. The explanation which suggests itself is expressed in the following sequence of transformations:



The transformation expressed by the change of A into B is the fundamental one of our theory, leading to a carbonium ion B; the migration of H₃C: to the positive carbon of the carbonium ion is also a normal phase of the rearrangement according to the theory;

the new feature is the migration of an ethyl radical $C_2H_5\cdot$ to the positive carbon atom of the new carbonium ion C, before the free radical type of breakdown occurs, as expressed in the change of D into E of the type discussed above. The result of these transformations is a virtual exchange of a methyl and an ethyl radical, but, it should be emphasized, not in a simultaneous action but in a sequence of migrations to a free positive charge of a carbonium ion. That is clearly a possibility within the range of the electrical forces forming the basis of the theory under investigation.

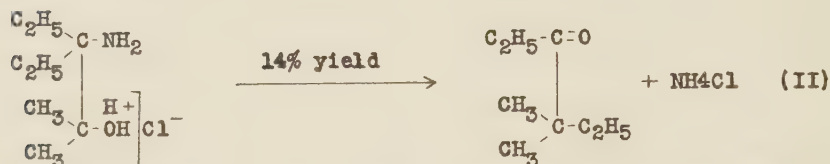
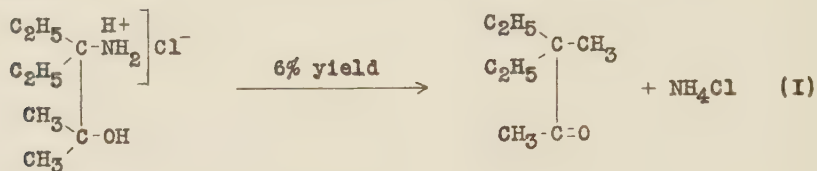
It is evident that the same sequel of reactions might have started by a decomposition of the carbinol oxonium ion into a carbonium ion by the loss of water. It would lead, mutatis mutandis, to the same final products.

No evidence of a secondary butyl chloride, $CH_3CH_2CHClCH_3$, or its decomposition product, representing a butylene C_4H_8 , was found in the oil; but there were some fractions that were not identified, including a polymeric hydrocarbon $C_{12}H_{24}$ with a single double bond, as will presently be reported. (See also p.47 in regard to the presence of high boiling chlorides.)

Whatever interpretation of the formation of methyl ethyl ketone may ultimately be found correct, its positive identification proves beyond question that it represents a decomposition in which the final ketone carbon atom has lost an alkyl (CH_3 or C_2H_5) and has gained another alkyl (C_2H_5 or CH_3). Exhaustive investigation of the by-products of pinacol rearrangements may well reveal further instances of this sequence of migrations.

(4) Dimethylethylmethyl ethyl ketone and diethylmethylmethyl methyl ketone. - These two ketones were found to be produced in about a fourteen and a six per cent yield, respectively. The preponderance of the ethyl ketone over the methyl ketone would

indicate an approximately two-fold greater tendency to rearrangement at the alcohol group, as can be illustrated in the following manner:



Due to the fact that an amine is a very much stronger base than an alcohol, one would say that the concentration of the substituted ammonium ion is much greater than the concentration of the oxonium ion. That factor, according to the Stieglitz theory, decidedly favors reaction (I). At the same time alkyl ammonium salts are by far more stable compounds than oxonium salts; the former do not suffer decomposition, for instance, into ammonia and alkyl halides, at all at ordinary temperatures, whereas carbinols, and especially tertiary carbinols, react measurably fast even at room temperatures with halogen acids to form alkyl halides and water. With the use of heat, complete and very speedy action takes place at far lower temperatures in the case of the carbinols than with the amines. This factor of thermal instability very greatly favors reaction (II). Judged by the experimental result, the second factor not only overcomes the unfavorable factor of the weaker affinity of the carbinol basic group for the acid but gives reaction (II) the advantage. It is to be noted that in these conclusions no consideration is taken of the relative electronegativity of alkyl groups.

It must be further concluded, that at the rearrangement temperature used (195° - 200°), the tendency for decomposition reactions to occur is a major one, affecting, in fact, about eighty per cent of the material.

(5) High-boiling unsaturated hydrocarbons. - A mixture of unsaturated hydrocarbons boiling above 160° was obtained, which corresponded to about thirty per cent of the original alkamine hydrochloride. Evidence of unsaturation was found in its reaction with bromine. When further fractionated this mixture gave indications of the following compounds, each containing one double bond: $C_{12}H_{24}$, $C_{14}H_{28}$ and $C_{15}H_{30}$.

The water layer remaining after the rearrangement was found to contain ammonium chloride and some unchanged alkamine hydrochloride.

When the rearrangement of the alkamine hydrochloride was carried out in the presence of twice its weight of hydrochloric acid (3N) at 195° - 200° , the products obtained and their proportions as far as the rearrangement is concerned were practically identical with those obtained from rearrangement of the hydrochloride in water solution. The proportion of the methyl ketone to the ethyl ketone was approximately 6% to 15%, in place of 6% to 14%.

It was noticed that the same volume of the water-insoluble layer was formed in about one-half the time in 3N hydrochloric acid, as compared with the water solution, indicating an acceleration both of the rearrangements and of the secondary reactions. The high-boiling olefine fraction was found to contain considerable amounts of chloride even after distillation over solid potassium carbonate. Any removal of hydrochloric acid by unsaturated

hydrocarbons would lead to a decrease in acceleration of that expected of the original acid concentration.

On the basis of this work and other work done in this laboratory and of the result of investigations of others discussed in Part I, we may now summarise our conclusions concerning some of the factors controlling the course of the rearrangement of pinacols and of alkamines of the pinacol type:

1. Where nitrous acid brings about a rearrangement of an alkamine, the migrating group goes exclusively to the carbon atom originally holding the amine group. This is because nitrous acid converts only amines through a diazo compound into rearranging carbonium ions.

2. When an alkamine is rearranged by an acid, two factors determine the course of migration: (a) The stronger basic properties of the carbamine group give it the preference over the carbinol group in binding the acid used to bring about the rearrangement. (b) Oxonium salts of carbinols have a far lower decomposition point, involving the loss of water and the formation of carbonium ions than is shown by alkylammonium salts to lose ammonia and produce carbonium ions. Rearrangement by way of a carbinol group has therefore very great advantages in the comparatively low temperatures required and in the greater speed of rearrangement at any temperature.

3. When only one equivalent of acid is used on the alkamine, rearrangement requires the high temperature and shows the relatively low speed characteristic of a rearrangement through an alkylammonium ion; but, as found in the present study, the high temperature also greatly accelerates rearrangement through the carbinol group. (This result must be checked by a longer series of experiments.)

4. In the presence of excess of acid, the greater ease of rearrangement through the oxonium salt of a carbinol, makes itself plainly manifest. Adams found a ten-fold excess of acid accelerates the rearrangement of the alkamine, tetramethyl-2-amino ethanol, $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{C}(\text{OH})(\text{CH}_3)_2$, eight to nine fold.

5. By decreasing the stability of the alkammonium ion (e.g. by substituting C_6H_5 etc. for H in the amine group) the temperature of rearrangement of this ion may be appreciably lowered which in view of the greater basic strength, compared with the carbinol group, would favor the course of rearrangement through the amino-carbon group as against rearrangement through the carbinol group.

6. In the rearrangement of pinacols there should likewise be two primary factors, first, the relative basic strength (affinity for H) of the carbinol groups and, second, the ease of decomposition of the oxonium ions with the formation of the rearranging carbonium ions. The second factor might easily be the predominating one.

7. The relative negativity of radicals (alkyls, aryls, H) attached to the tertiary carbon atoms in unsymmetrical molecules probably affects the rearrangement by its influence on the basic character and chiefly, on the stability of the carbon-hydroxyl bond, thus facilitating the formation of carbonium ions. It is the location of the positively charged carbonium ion that determines the subsequent course of the rearrangement.

8. For the comparison of the ease of migration of two radicals R and R_1 , it evidently is necessary to use the symmetrical pinacols $\text{RR}_1\text{C}(\text{OH})\text{C}(\text{OH})\text{RR}_1$, where R and R_1 have equal chances to

migrate in reference to the location of the positive charge of the carbonium ion. This consideration evidently explains the conclusion of Bachman and Sternberger that alkyl groups migrate differently when situated in the two types of pinacols,

$RR_1C(OH)C(OH)R_1R_1$, and $RR_1C(OH)C(OH)RR_1$.

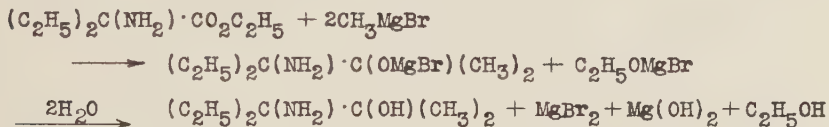
9. In the current investigation the first indications were obtained of a double migration, as a result of which one alkyl group replaces another one (see p. 22).

10. Decomposition of pinacols and alkamines of the pinacol type into free radicals and their oxidation-reduction products is being recognized more and more frequently as accompaniments of rearrangements.

IV. EXPERIMENTAL PART

* * *

(c) 1,1,1 Dimethylhydroxy-2,2 diethyl-2-amino ethane,
 $(\text{CH}_3)_2\text{C}(\text{OH}) \cdot \text{C}(\text{NH}_2)(\text{C}_2\text{H}_5)_2$:- This alkamine was prepared according to the following reactions:



A Grignard solution was prepared by the slow addition, with stirring, of 100 g. of methyl bromide, dissolved in 250 cc. of pure anhydrous ether, to a mixture consisting of 24 G. of granulated magnesium metal and 100 cc. of ether. The stirring was continued for an additional hour. The solution was then filtered, by gravitation, through an asbestos thimble; the filtering system was kept at atmospheric pressure, and protected from moisture, by means of two calcium chloride tubes. To this filtrate was added slowly, with stirring, a solution of 40 g. of α -amino diethyl acetic acid ethyl ester in 100 cc. of ether. The mixture was stirred for an additional two hours and then hydrolyzed with ice water. The ether was removed by distillation and the remaining mixture heated on a steam bath for four or five hours, whereupon it was steam distilled, about one liter of distillate being collected. The distillate was acidified with hydrochloric acid and evaporated to a thick syrup. The ether extracts were dried for two hours over powdered sodium hydroxide. Upon removal of the ether by distillation, and fractionation of the remaining residue at 10 mm., about 10 g. of the desired alkamine was obtained,

boiling at 74.5°-76.5° at 10 mm. The alkamine was titrated against 0.1005 N hydrochloric acid, methyl orange being the indicator:

cc. 's of 0.1005 N HCl		
Calc. for $C_8H_{19}ON$		Found
0.3056 g. required.....	20.96	20.93
0.5127 g. "	35.20	35.20

Micro-analysis (Pregl) of the alkamine gave:

Sub. 3.256 mg.: CO_2 7.902 mg. H_2O 3.826 mg.
 Calc. for $C_8H_{19}ON$: C, 66.2% H, 13.20%
 Found: C, 66.2% H, 12.97%
 Sub. 3.605 mg., 4.202 mg.: 0.316 cc. N_2 (26°, 749 mm.),
 0.363 cc. N_2 (26.5°, 749 mm.)
 Calc. for $C_8H_{19}ON$: N, 9.65%.
 Found: N, 9.87, 9.69%

(d) 1,1,1 Dimethylhydroxy-2,2 diethyl-2-amino ethane chloroplatinate, $(C_8H_{20}ON)_2PtCl_6$:- About 20 mg. of chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$, was dissolved in 2 cc. of absolute alcohol and the solution filtered. To this clear filtrate was added 10 to 15 mg. of 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane, $(C_2H_5)_2C(NH_2) \cdot C(OH)(CH_3)_2$, and about 1 cc. of dry ether. The precipitate of the chloroplatinate was removed by filtration and washed twice with 1 cc. portions of dry ether; the melting point was 186°-188°.

Micro-analysis gave:

Sub. 5.431 mg.: Pt 1.499 mg.
 Calc. for $(C_8H_{20}ON)_2PtCl_6$: Pt, 27.93%
 Found: Pt, 27.6%

(e) 1,1,1 Dimethylhydroxy-2,2 diethyl-2-amino ethane hydrochloride, $[(CH_3)_2C(OH) \cdot C(NH_3^+)(C_2H_5)_2]Cl^-$:- About 10 g. of the pure alkamine was dissolved in 30 cc. of pure dry ether and dry hydrogen chloride gas bubbled through this solution until precipitation was complete. The precipitate was separated by

filtration, washed twice with dry ether and allowed to remain, for 3 or 4 days, in a vacuum desiccator, containing solid potassium hydroxide; the melting point was 153° - 155° .

Analysis for ionizable chlorine gave:

Sub. 0.2892 g., 0.3105 g.: AgCl .2140 g., .2462 g.

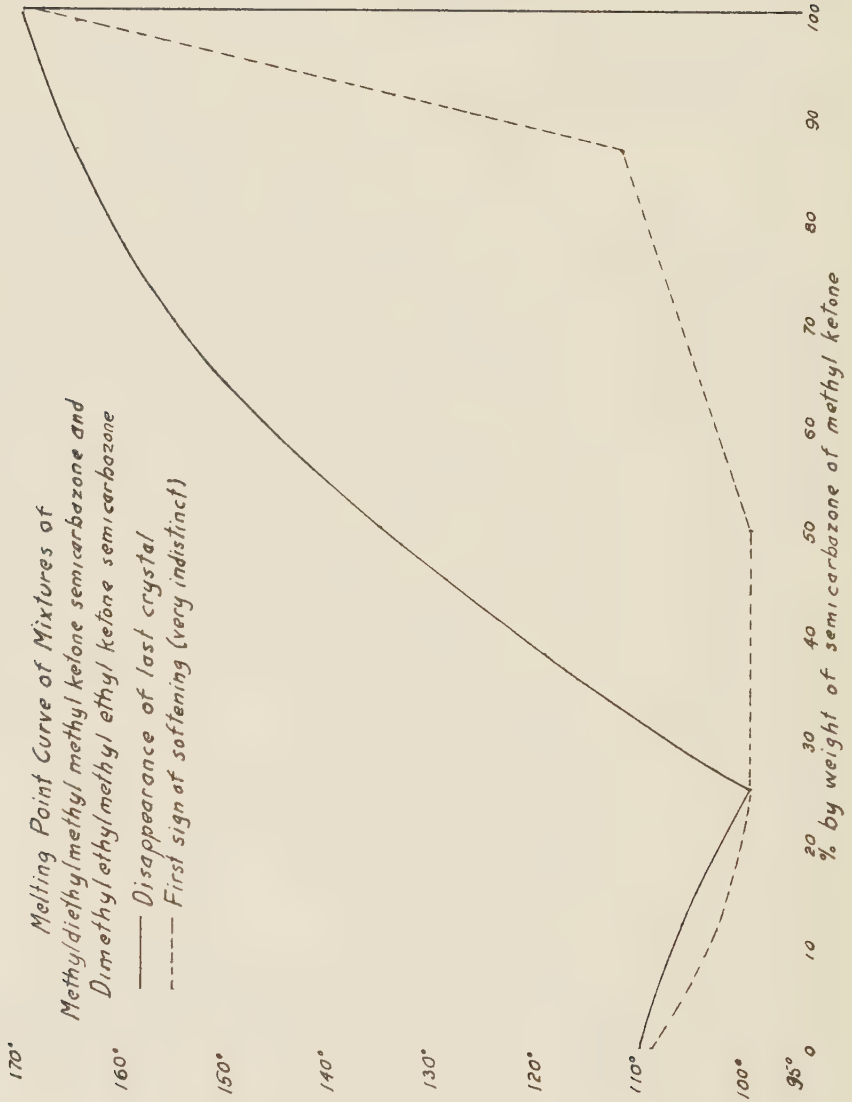
Calc. for $C_8H_{20}ON$ Cl: Cl, 19.55%.

Found: Cl, 19.65, 19.61%

* * *

6. A semi-quantitative determination of mixtures of dimethylethylmethyl ethyl ketone, $(CH_3)_2(C_2H_5)C \cdot COC_2H_5$, and methyldiethylmethyl methyl ketone, $CH_3(C_2H_5)_2C \cdot COCH_3$: - Various mixtures of the semicarbazones of these ketones were made with the aid of the micro-balance and the melting point of each of these mixtures determined. The first sign of melting and the disappearance of the last crystal were noted. The results were plotted in the accompanying diagram. By means of this diagram it was found possible to analyze mixtures of the semicarbazones with an accuracy of about 2%.

It was previously found that an 89% yield of methyldiethylmethyl methyl ketone semicarbazone and a 74% yield of dimethylethylmethyl ethyl ketone semicarbazone could be obtained from their respective ketones, both values being reproducible and accurate within about three per cent. These data and the melting point curve (see diagram) made it possible to analyze mixtures of the two ketones with an accuracy of approximately five per cent. In Table II (see p. 39) are recorded the results of four determinations on known mixtures of the ketones. The mixed semicarbazones were prepared from the proportions given for the



preparation of the pure semicarbazones. The melting point recorded was that temperature at which the very last crystal disappeared.

TABLE II

A SEMI-QUANTITATIVE DETERMINATION OF KNOWN MIXTURES OF
DIMETHYLETHYLMETHYL ETHYL KETONE AND
METHYLDIETHYLMETHYL METHYL KETONE

Sample	I	II	III	IV
Wt. of the methyl ketone..	0.24 g.	0.36 g.	0.13 g.	0.05 g.
Wt. of the ethyl ketone...	0.29 g.	0.15 g.	0.28 g.	0.40 g.
Wt. of the mixed semicarbazones.....	0.60 g.	0.62 g.	0.43 g.	0.48 g.
Melting point of the mixed semicarbazones....	135°-136°	155°-156°	115°-116°	106°-107°
Methyl ketone (%), Theory.	45	71	32	11
Found..	44	70	29	10
Ethyl ketone (%) Theory.	55	29	68	89
Found..	53	30	63	88

7. Rearrangement of 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane hydrochloride, $[(CH_3)_2C(CH) \cdot C(NH_3^+)(C_2H_5)_2]Cl$, in water solution at 195°-200°: - A solution of 10 g. of the alkamine hydrochloride in 20 cc. of water was heated in a bomb tube for 7 hours at 195°-200°. At the end of this time an oily layer had collected upon the surface of the water solution. The two layers were separated in a small separatory funnel. The water layer was distilled, about 5 cc. of distillate being collected. This distillate was saturated with potassium carbonate, and the oily layer thus formed, separated and combined with the one above. The combined oily material was dried over anhydrous potassium carbonate and then fractionated. The results of two

fractionations are recorded in Table III (see below). The analysis of the fractions from the second fractionation are given as follows:

TABLE III

REARRANGEMENT OF 1,1,1 DIMETHYLHYDROXY-2,2 DIETHYL-2-AMINO ETHANE HYDROCHLORIDE, IN WATER SOLUTION AT 195°-200°

1st fractionation				2nd fractionation			
No.	Temp.	Press.	Wt.	No.	Temp.	Press.	Wt.
1	30°-50°	760 mm.	0.3 g.	13	32°-42°	760 mm.	0.2 g.
2	50°-70°	"	0.3 g.	14	50°-60°	"	0.2 g.
3	70°-90°	"	0.3 g.	15	75°-85°	"	0.2 g.
4	90°-120°	"	0.3 g.	16	125°-135°	"	0.5 g.
5	120°-140°	"	0.7 g.	17	140°-160°	"	1.5 g.
6	140°-160°	"	1.7 g.	18	70°-80°	10 mm.	0.4 g.
7	55°-75°	10 mm.	0.4 g.	19	100°-115°	"	0.4 g.
8	75°-95°	"	0.5 g.	20	115°-130°	"	0.3 g.
9	95°-105°	"	0.4 g.				
10	105°-125°	"	0.4 g.				
11	125°-145°	"	0.3 g.				
12	above 145°	"	0.2 g.				

(1) 2,3-n-Amylene:- The boiling point of this fraction No. 13) was 32°-42°.

Micro-analysis gave:

Sub. 2.845 mg.: CO₂, 8.901 mg. H₂O, 3.580 mg.

Calc. for C₅H₁₀: C, 85.7% H, 14.3%

Found: C, 85.4% H, 13.9%

A micro molecular weight determination, by the air displacement method of Victor Meyer, gave:

Sub. 10.3 mg.: 3.59 cc. of air (26°, 751 mm.) displaced

Calc. for C₅H₁₀: Mol. Wt., 70

Found: Mol. Wt., 71

The compound was found to be unsaturated. A weighed amount was added to about 0.5 cc. of carbon tetrachloride, and to this solution was added, at about 0°, a bromine solution

(0.31 molar) in carbon tetrachloride until the color of the bromine no longer disappeared within about one minute. The bromine solution was added from a small graduated pipette.

Sub. 12.7 mg.: 0.62 cc. of Br_2 sol. (0.31 molar) in CCl_4

Calc. for C_5H_{10} : Br_2 required, 29.0 mg.

Found: Br_2 required, 31.0 mg.

From these data it was decided that the hydrocarbon was one of the amylenes. Of the possibilities:

- | | | | |
|-----|--|-------|---------------------------------|
| (1) | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}:\text{CH}_2$, | b. p. | $39^\circ\text{--}40^\circ$ |
| (2) | $\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_3$, | " | 36.5° |
| (3) | $(\text{CH}_3)_2\text{CHCH}:\text{CH}_2$, | " | $21.1^\circ\text{--}21.3^\circ$ |
| (4) | $\text{CH}_3(\text{C}_2\text{H}_5)\text{C}:\text{CH}_2$, | " | $31^\circ\text{--}32^\circ$ |
| (5) | $(\text{CH}_3)_2\text{C}:\text{CHCH}_3$, | " | 37.1° |

(3) and (4) were eliminated because their boiling points were too low, and because oxidation of the unknown, with hot alkaline permanganate, showed no evidence of isobutyric acid and with cold neutral permanganate, showed no evidence of methyl ethyl ketone, respectively. Compounds (1) and (5) were eliminated for these same latter two reasons, no evidence being shown for the presence, after oxidation, of butyric acid or acetone,⁴⁸ respectively. Oxidation of the unknown did show evidence of acetic acid, as detected by its odor and the formation of cacodyl, $(\text{CH}_3)_4\text{As}_2$, which further supports formula (2) for the unknown.

(2) Acetone:— The boiling point of this fraction (No. 14) was $50^\circ\text{--}60^\circ$. It possessed a decided odor of acetone. When a few drops of this material were added to a saturated solution of p-nitrophenylhydrazine, in 40% acetic acid, very beautiful yellow needles of the p-nitrophenylhydrazone formed easily. After

⁴⁸Wagner, Ber., 21, 1235 (1888).

recrystallization from a water-alcohol (3:1) mixture, the crystals melted at 147°-148°. The melting point of acetone p-nitrophenylhydrazone, $(CH_3)_2C:NNHC_6H_5NO_2$, prepared from pure acetone, was found to be 147°-148°. The melting point of a mixture (1:1) of these two specimens of p-nitrophenylhydrazone was found to be 147°-148°. The recorded melting point of acetone p-nitrophenylhydrazone is 148°-148.5°.⁴⁹

Micro-analysis gave:

Sub. 2.985 mg.: CO_2 , 6.081 mg. H_2O , 1.537 mg.

Calc. for $C_9H_{11}O_2N_3$: C, 55.8% H, 5.69%

Found: C, 55.6% H, 5.68%

Sub. 3.010 mg.: N_2 , 0.582 cc. (27°, 753 mm.)

Calc. for $C_9H_{11}O_2N_3$: N, 21.75%

Found: N, 21.8%

(3) Methyl ethyl ketone:— The boiling point of this fraction (No. 15) was 75°-85°. It possessed an odor resembling acetone. It formed yellow needles of the p-nitrophenylhydrazone very easily. The melting point, after repeated recrystallization of the compound from a water-alcohol (3:1) mixture, was found to be 120°-121°. The melting point of methyl ethyl ketone p-nitrophenylhydrazone, $CH_3(C_2H_5)C:NNHC_6H_5NO_2$, prepared from pure methyl ethyl ketone, was found to be 120°-121°. The melting point of a mixture (1:1) of these two specimens of p-nitrophenylhydrazone was found to be 120°-121°. The recorded melting point of methyl ethyl ketone p-nitrophenylhydrazone is 119.5°-120°.⁵⁰

Micro-analysis gave:

Sub. 3.414 mg.: CO_2 , 7.257 mg. H_2O , 1.953 mg.

⁴⁹Bamberger and Sternitzki, Ber., 26, 1306 (1893).

⁵⁰Bulow and Deiglmayr, Ber., 37, 1793 (1904).

Calc. for $C_{10}H_{13}O_2N_3$: C, 57.9% H, 6.28%

Found: C, 58.0% H, 6.31%

Sub. 2.563 mg.: N, 0.461 cc. (27.5°, 753 mm.)

Calc. for $C_{10}H_{13}O_3N_2$: N, 20.3%

Found: N, 20.2%

(3) The boiling point of this fraction (No. 16) was 125°-135°.

Micro-analysis gave:

Sub. 4.717 mg.: CO_2 , 13.09 mg. H_2O , 5.350 mg.

Found: C, 75.6% H, 12.5%

Molecular weight determination (Victor Meyer) gave:

Sub. 9.3 mg.: 1.76 cc. of air (25°, 749 mm.) displaced.

Found: Mol. Wt., 131.

This material was found to react with about one-third of the bromine required for one double bond, indicating a mixture. Phenylhydrazine, p-nitrophenylhydrazine and semicarbazine gave only a slight ketone reaction.

(4) Dimethylethylmethyl ethyl ketone, $(CH_3)_2(C_2H_5)C \cdot COC_2H_5$, and methyldiethylmethyl methyl ketone, $CH_3(C_2H_5)_2C \cdot COCH_3$: - The boiling point of this fraction (No. 17) was 140°-160°. This material (1.5 g.) gave 1.5 g. of the mixed semicarbazones. In melting the last crystal disappeared at 112°, which represented a mixture of approximately 33% of methyldiethylmethyl methyl ketone semicarbazone and 67% of dimethylethylmethyl ethyl ketone semicarbazone. These data represented a yield of about 0.4 g. of methyldiethylmethyl methyl ketone and 1.0 g. of dimethylethylmethyl ethyl ketone or a 6% and a 14% yield, respectively, from 10 g. of the alkamine hydrochloride.

Micro-analysis of the mixed semicarbazones gave:

Sub. 3.763 mg.: CO_2 , 8.035 mg. H_2O , 3.447 mg.

Calc. for $C_9H_{19}ON_3$: C, 58.3% H, 10.3%

Found: C, 58.2% H, 10.1%

(6) The boiling point of this fraction (No. 18) was 70° - 80° at 10 mm.

Micro-analysis gave:

Sub. 2.022 mg.: CO_2 , 6.335 mg. H_2O , 2.564 mg.

Calc. for $C_{12}H_{24}$: C, 85.7% H, 14.3%

Found: C, 85.4% H, 14.0%

Molecular weight determination gave:

Sub. 12.03 mg.: 0.177 cc. of air (27° , 746 mm.) displaced

Calc. for $C_{12}H_{24}$: Mol. Wt., 168 Found: 170.

Addition of bromine gave:

Sub. 15.5 mg.: 0.28 cc. of Br_2 sol. (0.31 molar) in CCl_4

Calc. for $C_{12}H_{24}$ (one double bond): Br_2 required, 14.8 mg.

Found: " , 14.0 mg.

From these data it was concluded that this fraction consisted of a hydrocarbon, $C_{12}H_{24}$, containing one double bond.

(7) The boiling point of this fraction (No. 19) was 100° - 115° at 10 mm.

Micro-analysis gave:

Sub. 1.988 mg.: CO_2 , 6.212 mg. H_2O , 2.562 mg.

Calc. for $C_{14}H_{28}$: C, 85.7% H, 14.3%

Found: C, 85.2% H, 14.2%

Molecular weight determination gave:

Sub. 10.7 mg.: 0.142 cc. of air (29° , 746 mm.) displaced

Calc. for $C_{14}H_{28}$: Mol. Wt., 196 Found: 190

Addition of bromine gave:

Sub. 20.2 mg.: 0.29 cc. of Br_2 sol. (0.31 molar) in CCl_4

Calc. for $C_{14}H_{28}$ (one double bond): Br_2 required, 16.5 mg.

Found: required, 14.5 mg.

From these data it was concluded that this fraction consisted of a hydrocarbon, $C_{14}H_{28}$, containing one double bond.

(8) The boiling point of this fraction (No. 20) was 115° - 130° at 10 mm.

Micro-analysis gave:

Sub. 2.136 mg.: CO_2 , 6.680 mg. H_2O , 2.693 mg.

Calc. for $C_{15}H_{30}$: C, 85.7% H, 14.3%

Found: C, 85.3% H, 13.9%

Molecular weight determination gave:

Sub. 13.3 mg.: 0.166 cc. of air (30° , 748 mm.) displaced

Calc. for $C_{15}H_{30}$: Mol. Wt., 210 Found 203

Addition of bromine gave:

Sub. 25.3 mg.: 0.33 cc. of Br_2 sol. (0.31 molar) in CCl_4

Calc. for $C_{15}H_{30}$ (one double bond): Br_2 required, 19.3 mg.

Found: " , 16.5 mg.

From these data it was concluded that this fraction consisted chiefly of a hydrocarbon, $C_{15}H_{30}$, containing one double bond.

The water layer from the original rearrangement mixture was evaporated to dryness. The residue weighed 3.6 g. It was extracted with absolute alcohol. The residue, which remained after this extraction, weighed 2.8 g. and was found to consist of ammonium chloride. The alcohol extract was evaporated and this residue dissolved in 10% sodium hydroxide. The oily layer, which formed, was separated and distilled. No definite fraction was obtained. The largest fraction, which boiled at 50° - 100° at 10 mm., very likely consisted of unchanged alkamine.

8. Rearrangement of 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane hydrochloride, $[(CH_3)_2C(OH) \cdot C(NH_3^+)(C_2H_5)_2] Cl^-$, in hydrochloric acid (3N) at 195°-200°: - A solution of 10 g. of the alkamine hydrochloride in 20 cc. of 3N hydrochloric acid was heated in a bomb tube for 4 hours at 195°-200°. The same fractions, in practically the same proportions, were obtained as in the rearrangement of the alkamine hydrochloride in water solution (see p. 41), with the following exceptions:

Fraction (17):- The boiling point of this fraction was 140°-160°. This material (1.6 g.) gave 1.5 g. of the mixed semicarbazones. In melting the last crystal disappeared at 107°, which represented a mixture of approximately 31% of methyldiethylmethyl methyl ketone semicarbazone and 69% of dimethylethylmethyl ethyl ketone semicarbazone. These data represented a yield of about 6% of methyldiethylmethyl methyl ketone and about 15% of dimethylethylmethyl ethyl ketone.

Micro-analysis gave:

Sub. 3.606 mg.: CO_2 , 7.710 mg. H_2O , 3.305 mg.

Calc. for $C_9H_{19}ON_3$: C, 58.3% H, 10.3%

Found: C, 58.3% H, 10.1%

Fractions (18), (19) and (20):- These fractions were obtained by the distillation of the original fractions from powdered potassium hydroxide, and showed the presence of considerable amounts of a chloride.

V. SUMMARY

1. A new alkamine, 1,1,1 dimethylhydroxy-2,2 diethyl-2-amino ethane, $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{NH}_2)(\text{C}_2\text{H}_5)_2$, was prepared.

2. A semi-quantitative method for the analysis of mixtures of methyldiethylmethyl methyl ketone, $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{C}\cdot\text{COCH}_3$, and dimethylethylmethyl ethyl ketone, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{C}\cdot\text{COC}_2\text{H}_5$, by the use of a melting point curve of mixtures of their semicarbazones, was developed.

3. The alkamine hydrochloride was rearranged in both a water solution and a hydrochloric acid (3N) solution, a temperature of 195° - 200° being used in each case. In water solution about 6% of methyldiethylmethyl methyl ketone and about 14% of dimethylethylmethyl ethyl ketone were formed, and in hydrochloric acid about 6% and 15% of the ketones, respectively, were formed. This indicates, in both solutions, a greater tendency for carbonium ion formation at the carbinol carbon atom than at the amine carbon atom.

4. Acetone and 2,3-n-amylene were identified among the products of rearrangement. They were most likely formed by a scission of the bond between the tertiary carbon atoms of the alkamine.

5. Methyl ethyl ketone was identified from the products of the rearrangement. The formation of this ketone may represent a new type of rearrangement, in which a methyl and an ethyl radical exchange position, presumably not in one simultaneous action, but in a sequence of migrations to a free positive charge of a

carbonium ion; these changes are apparently followed by a scission of the tertiary carbon atoms of the pinacol.

6. Three high boiling hydrocarbons, containing one double bond, were identified from the products of the rearrangement. The high boiling mixture, some of whose components were not identified, corresponded to about thirty per cent of the alkamine.

